

NOVEL ORGANOMETALLIC LUMINESCENT MATERIALS AND
ORGANIC ELECTROLUMINESCENT DEVICE CONTAINING SAME

CROSS-REFERENCE TO RELATED APPLICATION

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This application is a *continuation-in-part* of U.S. patent application Ser. No. 09/336,713, filed on June 21, 1999, now abandoned.

10 FIELD OF THE INVENTION

The present invention is directed to a novel organometallic luminescent material, and more particularly, to a novel organometallic luminescent material having the capability of emitting pure blue light and high thermal stability, and an organic electroluminescent device(OELD) containing same.

BACKGROUND OF THE INVENTION

20 Conventional organometallic luminescent compounds used in organic electroluminescent devices are mostly complexes of divalent or trivalent metals such as zinc and aluminum.

For example, U.S. Patent No. 5,456,988 describes 8-hydroxyquinoline complexes of zinc, aluminum and magnesium 25 as organic luminescent materials; U.S. Patent No. 5,837,390 discloses magnesium, zinc and cadmium complexes of 2-(o-hydroxyphenylbenzoxazole); Japanese Patent Laid-Open Publication No. 07-133483 reports luminescent complexes of 2-(o-hydroxyphenylbenzoxazole) with divalent metals such as

magnesium and copper; and U.S. Patent No. 5,529,853, and Japanese Patent Laid-Open Publication Nos. 06-322362, 08-143548 and 10-072580 disclose divalent or trivalent metal complexes of 10-hydroxybenzo[10]quinoline.

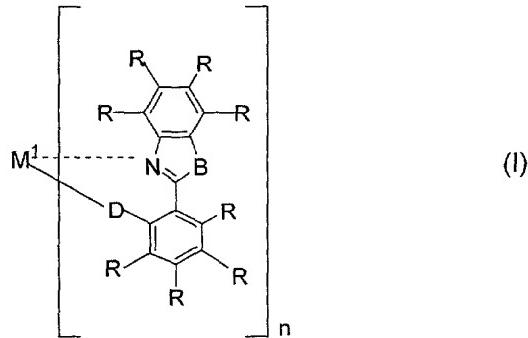
5 The above organometallic luminescent compounds containing a divalent or trivalent metal have relatively loosely-bound ligands and an extended system of conjugation. As a result, they are relatively unstable and emit green or red light but not blue light.

10 Therefore, there has existed a need to develop an organometallic luminescent material having an improved stability and light emission characteristics such as the capability of emitting pure blue light.

15 SUMMARY OF THE INVENTION

Accordingly, it is a primary object of the present invention to provide a novel organometallic luminescent material having good stability and desired emission characteristics, and an 20 organic luminescent device containing same.

In accordance with the present invention, there is provided an organometallic luminescent complex of formula (I).



wherein,

M¹ is a monovalent or tetravalent metal selected from the group consisting of Li, Na, K, Zr, Si, Ti, Sn, Cs, Fr, Rb, Hf, Pr, Pa, Ge, Pb, Tm and Md;

5 R is hydrogen or C₁₋₁₀ alkyl;

B is O, S, Se or Te;

D is O or S; and

n is an integer ranging from 1 to 4.

10 BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects and features of the present invention will become apparent from the following description thereof, when taken in conjunction with the accompanying drawings
15 wherein:

Figures 1a, 1b and 1c illustrate schematic diagrams of organic electroluminescent devices having single-layered, double-layered and multi-layered organic interlayers, respectively, Figure 1d, energy band diagrams of OELDs, and
20 Figure 1e, chemical structures of (a)m-MTDATA, (b)NPB, (c)LiPBO, (d)BCP and (e)Alq3;

Figure 2 shows the light emission spectrum of the organometallic luminescent material obtained in Preparation 1 of the present invention;

25 Figure 3 represents thermal stabilities of the LiPBO obtained in Preparation 1 and a DPVBi powder;

Figure 4 exhibits the electroluminous spectra of the electroluminescent device obtained in Preparation 4 of the present

invention;

Figure 5 shows CIE color coordinate of the blue OELD-B1 in a multi-layered structure;

Figure 6 demonstrates variations of the current density(A/m²) and luminance(cd/m²) of the electroluminescent devices obtained in Preparation 6 of the present invention as function of applied voltage(V); and

Figure 7 depicts changes in the luminous efficiencies(cd/A) with luminance(cd/A) of the OELD-B1 (filled circle), OELD-B2 (open rectangle) and OELD-B3 (open triangle) obtained in Preparation 6.

DETAILED DESCRIPTION OF THE INVENTION

15 The organometallic luminescent materials of the present invention include benzoxazole- or benzthiazole- metal complexes of formula (I).

Among the organometallic luminescent materials of the present invention, preferred are those listed in Table I.

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Table I

Compound No.	M ¹	B	D	N	R	λ _{max} (nm)	color
1	Li	O	O	1	H	450	blue
2	Na	-	O	1	H	455	blue

Compound 1, 2-(2-hydroxyphenyl)benzoxazol-lithium(LiPBO) can be applied as a stable blue emission layer in an organic 25 electroluminescent device(OELD) because it has a high glass transition temperature of more than 200°C.

The organometallic luminescent compound of the present invention may be prepared by reacting an organic compound that can serve as a ligand with an appropriate metal compound in a suitable solvent.

5 Exemplary solvents which can be used in the present invention include water, ethanol, methanol and propanol.

Representative metal compounds that can be used to prepare the organometallic luminescent compounds of the present invention are LiOH, NaOH, KOH, NaCl, KCl, LiCl, ZrCl₄, SnCl₄, TiCl₄, SiCl₄, 10 BeCl₂, MgCl₂, AlCl₃, CaCl₂ and ZnCl₂.

Representative organic compounds which can be used as ligands in the present invention include 2-(2-hydroxy-phenyl) benzoxazole and 2-(2-hydroxy-phenyl)benzthiazole.

The reaction of the organic and metal compounds to prepare 15 the organometallic luminescent compound of the present invention may be carried out in stoichiometric amounts, which depend on n, at a temperature ranging from 25 to 100°C for 1 to 24 hours.

The organometallic complex of the present invention can be used as a luminescent doping material as well. For example, 20 when it is doped in an amount of about 2% in a blue light emitting luminescent layer, the emitting light changes from blue to light blue or green. Accordingly, an efficient electroluminescent device capable of emitting a tuned color can be prepared.

The organic luminescent device of the present invention 25 comprises an organic interlayer which may be in the form of a single layer, in the form of a double layer containing a hole transporting layer(HTL) or an electron transporting layer(ETL) in addition to the light emitting luminescent layer, or in the

form of a multi layer containing still additionally a hole injecting layer(HIL) or a hole blocking layer(HBL). The organometallic luminescent material of the present invention can be used alone, or in combination with a polymer or an inorganic material. Further, it may be doped in a polymer to give a fluorescent thin layer.

An example of the electroluminescent device of the present invention contains a single organic layer as shown in Figure 1a. The device consists of (i) a glass substrate, (ii) a transparent ITO(indium tin oxides) anode electrode layer, (iii) an organic luminescent layer containing the organometallic luminescent material of the present invention, and (iv) a metal cathode electrode layer. Another example of the inventive device has an additional hole transporting layer(iii-1) as shown in Figure 1b, or a multi-layered structure shown in Figure 1C, wherein (iii-2) denotes an additional electron transporting layer. The electroluminescent device of the present invention may be operated with either direct or alternative current, while the direct current is preferred.

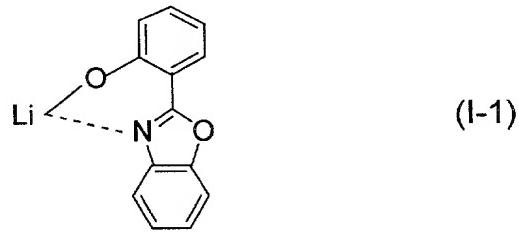
The organic luminescent layer of the present invention may be formed by a conventional method including a wet process such as spin coating, and a dry process such as a vapor deposition, vacuum thermal deposition, sputtering and electron beam deposition method.

The novel organometallic luminescent compound of the present invention is capable of emitting blue light, and in particular, the inventive complexes containing monovalent metals are stable even at a high temperature and emit bright blue light.

The present invention is further described and illustrated in Examples, which are however, not intended to limit the scope of the present invention.

5 Preparation 1: 2-(2-Hydroxyphenyl) benzoxazole-lithium (LiPBO)

2-(2-hydroxyphenyl)benzoxazole and lithium oxide were added to 250ml of ethanol in a molar ratio of 1:1 and the mixture was refluxed at 78°C for 4 hours. The reaction mixture was filtered and the solvent and moisture were removed under a reduced pressure 10 to give the titled compound of formula(I-1) (compound 1).



The compound thus obtained was analyzed by ICP-AES and EA, and the results are as follows:

Calculated => C: 71.95, H: 3.68, N: 6.44, O: 14.73, Li: 3.20

Found => C: 71.82, H: 3.95, N: 6.34, O: 13.94, Li: 3.95

Example 1: Photoluminescence spectrum and thermal stability of LiPBO

The light emission spectrum of the LiPBO complex thus obtained was measured and shown in Figure 2. The photoluminescence spectrum of the purified LiPBO film shows a maximum peak at 450nm.

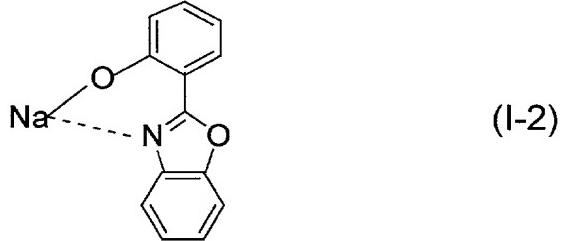
Also, the thermal stability of the purified LiPBO was examined by using differential scanning calorimeter(DSC). A second DSC run was performed to verify the scan is reproducible

after heating and cooling. For comparison, 4,4-bis(2,2-diphenylvinyl)biphenyl(DPVBi), which is known to be one of the best organic blue emitters, was also examined by DSC. The thermal relaxation behaviors of the LiPBO and a 5 DPVBi powder are shown in Figure 3. The glass transition temperature of the LiPBO and DPVBi were ca. 205°C and 385°C, respectively.

Preparation 2: 2-(2-Hydroxyphenyl)-benzoxazole-sodium (NaPBO)

10 2-(2-hydroxyphenyl)benzoxazole and NaOH were added to 250ml of ethanol in a molar ratio of 1:1 and the mixture was refluxed at 78°C for 4 hours. The reaction mixture was filtered and the solvent and moisture were removed under a reduced pressure to obtain the titled compound of formula (I-2) (compound 2).

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The maximum wavelength and emitted color of the complex thus obtained were 455nm and blue, respectively (Table I).

20 The compound thus obtained was analyzed by ICP-AES and EA, and the results are as follows:

Calculated => C: 66.96, H: 3.43, N: 6.00, O: 13.73, Na: 9.88

Found => C: 66.41, H: 3.20, N: 6.24, O: 14.04, Na: 10.11

Preparation 3: Tetra[2-(2-hydroxyphenyl)benzoxazolato]

25 zirconium(ZrPBO)

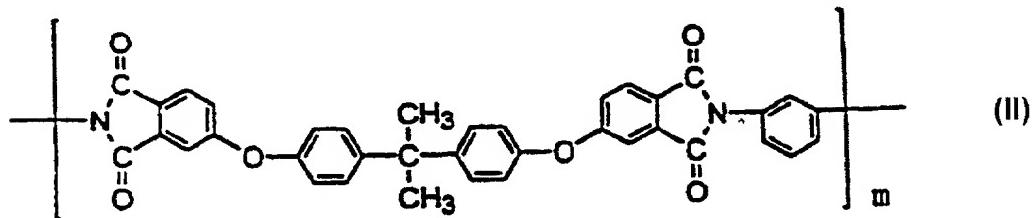
Preparation 1 was repeated except that zirconium chloride ($ZrCl_4$) was used instead of lithium to give the titled compound. The compound thus obtained was analyzed by ICP-AES and EA, and the results are as follows:

Calculated => C: 67.01, H: 3.44, N: 6.00, O: 13.75, Zr: 9.80
Found => C: 66.79, H: 3.63, N: 5.97, O: 13.69, Zr: 9.92

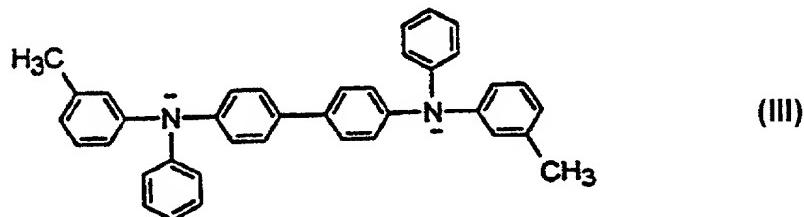
Preparation 4: Double-layered OELD

Indium-tin-oxide (ITO) was coated on a glass substrate to form a transparent anode layer. The coated substrate was subjected to photolithography and the patterned ITO glass was cleaned with a solution containing a non-phosphorous detergent, acetone and ethanol.

An equal weight mixture of polyetherimide of formula (II) and triphenylamine of formula (III) was dissolved in chloroform to a concentration of 0.5 wt%, and the resulting mixture was spin-coated on the ITO glass to form a hole transporting layer;



20



wherein m is an integer of two or higher.

On the hole transporting layer, 2-(2-hydroxyphenyl)benzoxazole-lithium(LiPBO) complex obtained in Preparation 1 was vapor deposited to a thickness of 20nm to form an organic luminescent layer, and then, aluminum was vapor deposited to 5 a thickness of 500nm to form a cathode layer on the organic luminescent layer. Subsequently, the device was packaged to obtain an organic electroluminescent device(OELD) having a double-layered structure as shown in Figure 1b.

10 **Example 2:** EL spectrum of OELD

Figure 4 exhibits electroluminous spectra of the OELD obtained in Preparation 4 observed at various applied voltages of 8, 9, 10, 11, 12 and 13V. The main peak appears at 456nm and shoulder peaks are observed at 430 and 487nm. The emitted 15 light was blue.

Preparation 5: Double-layered OELD

Preparation 4 was repeated except that ZrPBO with a thickness of 50nm was used as a luminescent material and Li:Al(Li content 20 0.15%) was used as a cathode layer to obtain an OELD having a double layer structure. The current injection started at ca. 3.5V. 24,300 cd/m² was achieved at 11V and the current density was 4,831 A/m². The luminous efficiency was 5.03 cd/A.

25 **Preparation 6:** Multi-layered OELD

Preparation 3 was repeated except that 4,4',4''-tris(N-3-methylphenyl-N-phenylamino)triphenylamine(m-MTDA), N,N'-diphenyl-N,N'-bis(1-naphthyl)-

(1,1'-biphenyl)-4,4'-diamine(NPB) and bathocuproine(BCP) were used in forming hole injecting layer(HIL), hole transporting layer(HTL) and hole blocking layer(HBL), respectively, to prepare three types(OELD-B1, OELD-B2 and 5 OELD-B3) each having a multi-layered structure.

OELD-B1 comprises a glass plate and layers of indium-tin oxide(ITO), 4,4',4"-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine(m-MTDATA)(200Å), N,N'-diphenyl-N,N'-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine(NPB or α -NPD)(75Å), 10 LiPBO(200Å), bathocuproine (BCP)(100Å), and Li:Al(1500Å).

OELD-B2 is composed of a glass plate and layers of ITO, m-MTDATA(200Å), NPB(100Å), LiPBO(200Å), tris(8-quinolinolato)aluminum(Alq3)(75Å), and Li:Al(1500Å).

Further, OELD-B3 had the layer structure of 15 glass/ITO/m-MTDATA(200Å)/NPB(100Å)/LiPBO(200Å)/BCP(50Å)/Alq3(50Å)/Li:Al(1500Å).

Energy band diagrams of the OELDs and chemical structures of the organic materials: (a)m-MTDATA, (b)NPB, (c)LiPBO, (d)BCP, and (e)Alq3 are shown in Figure 1d and 1e, respectively.

20 The luminescence characteristics of the OELD-B1, OELD-B2 and OELD-B3 are shown in Figures 6 and 7.

Example 3: CIE color coordinate of the OELD

The color purity of OELD-B1 was measured with the calibrated 25 candela meter(Minolta CS1000) and shown in Figure 5. As shown in Figure 5, the CIE color coordinate of the blue OELD is x=0.15 and y=0.08 at above 10,000 cd/m², which is the nearest value to the NTSC standard value of x=0.14 and y=0.08. In Figure 5,

open circles denote the NTSC standard blue, green and red values.

Example 4: Luminescence of OELD

Figure 6 illustrates variations of the current density (A/m^2)
5 and luminance (cd/m^2) of OELD-B1, OELD-B2 and OELD-B3 obtained
in Preparation 6 as function of the applied voltage (V). For
both OELD-B1 and OELD-B3, the current injection starts at ca.
3.5V. The maximum luminances of three OELDs are ca. $10,000 \text{ cd}/\text{m}^2$
or over, and in particular, ca. $14,600 \text{ cd}/\text{m}^2$, and $500 \text{ cd}/\text{m}^2$ can
10 be achieved with OELD-B3 at 11V.

Example 5: Efficiency of OELD

Figure 7 depicts changes in the luminous efficiencies (cd/A)
with luminance (cd/m^2) of OELD-B1, OELD-B2 and OELD-B3,
15 respectively. The luminous efficiency is steady at $1.2 \text{ lm}/\text{W}$
at a current density of $200\text{A}/\text{m}^2$ and beyond.

As can be seen from the above results, the organometallic
luminescent material of the present invention exhibits blue,
20 green or red light emission. Therefore, an electroluminescent
device containing the same is capable of exhibiting a full range
of colors in the visible region with a high efficiency.

While the embodiments of the subject invention have been
described and illustrated, it is obvious that various changes
25 and modifications can be made therein without departing from
the spirit of the present invention which should be limited
only by the scope of the appended claims.